

POLYMERIZATION STUDIES LEADING TO
HIGH STRENGTH CHEMICAL RESISTANT ELASTOMERS
SERVICEABLE AT TEMPERATURE EXTREMES

TECHNICAL REPORT
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(SEMIANNUAL REPORT NO. 5)

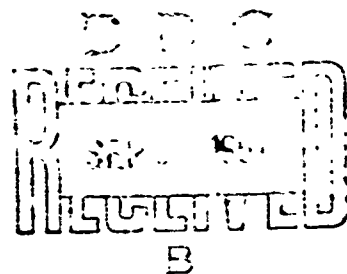
by

D. I. Relyea
H. P. Smith
A. N. Johnson

June 1967

Contract No. DA19-129-AMC-487(N)

U. S. ARMY NATICK LABORATORIES
NATICK, MASSACHUSETTS



UNIROYAL
UNITED STATES RUBBER COMPANY
RESEARCH CENTER
WAYNE, NEW JERSEY 07470

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for the period

December 1, 1966 - May 31, 1967

Contract No. DA19-129-AMC-487(N)
Project No. IK024401A113

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FOREWORD

This report describes work accomplished under Contract No. DA-19-129-AMC-487(N) between the United States Rubber Company (now UNIRROYAL, Inc.) and the U. S. Army Natick Laboratories. Mr. C. B. Griffis is the Project Officer. This is the fifth Semiannual Report under this contract and covers the period December 1, 1966 through May 31, 1967.

During the six-month period covered by this report, the following manhours were expended on this project:

| | |
|-------------------------------|---------------|
| Senior Research Scientist | 228 |
| Research Scientists | 1177 |
| Technician (Sub-professional) | <u>1470</u> |
| Total direct labor | 2985 manhours |

The technical effort for the past six months exceeded that required by the contract and brought the manhours total to 11940. This figure is 5% over the prorated contract requirement. We plan a 2200 manhour effort during the next six months.

SUMMARY

1. Rhodium trichloride in aqueous emulsion initiates the homopolymerization of 1,1,2-trifluorobutadiene (1) and 1,1,2-trifluoro-3-chlorobutadiene (2). Monomers 1 and 2 are also readily copolymerized with each other or individually with butadiene (4) to give rubbery polymers. The 51:49 1-4 copolymer has a Tg of -48°C. A sample has been furnished to U. S. Army Natick Laboratories for evaluation.
2. Preliminary experiments with iridium compounds indicate they are also active catalysts for polymerization of fluorinated dienes. Both rhodium and iridium are much less active with olefins and non-conjugated dienes.
3. Other new catalyst-monomer combinations have been explored. Among those which appear promising is a cobalt octoate-initiated copolymer of 2-(trifluoromethyl)butadiene and butadiene.
4. Monomers synthesized for use during this report period include 1, 2, 3,3,3-trifluoropropene, 2,3-bis(trifluoromethyl)butadiene, 5,5,5-trifluoro-4-trifluoromethyl-1,3-pentadiene, and 1,1,2,2-tetrafluoro-3-vinylcyclobutane.
5. Adducts of sulfenyl chlorides and cis-polybutadiene have been prepared with the following characteristics (sulfenyl chloride addend, % saturation in adduct, and Tg): CF_3SCl , 15%, -84°; CF_3SCl , 30%, -44°; $\text{C}_6\text{F}_5\text{SCl}$, 20%, -66°; $\text{C}_6\text{F}_5\text{SCl}$, 25%, -52°; and $\text{C}_6\text{Cl}_5\text{SCl}$, 15%, -50°. Samples of these adducts have been furnished to U. S. Army Natick Laboratories for evaluation.

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INTRODUCTION

This is the fifth semiannual report of research on the polymerization of fluorinated monomers to form random or stereospecific high polymers. This work, sponsored by the U. S. Army Natick Laboratories, has the objective of preparing new elastomeric materials which will be both oil- and chemical-resistant and have useful rubbery properties over a wide range of temperatures such as -65° to $+300^{\circ}\text{C}$.

During the period covered by this report we have explored the use of rhodium-containing catalysts as initiators of polymerization of fluorinated dienes and have continued to examine transition metal anionic coordination catalysts for both fluorinated olefins and fluorinated dienes. Additional samples of the adducts of sulfenyl chlorides to cis-polybutadiene have been prepared for continued evaluation at the U. S. Army Natick Laboratories.

DISCUSSION

1. Introduction

In our search for novel fluorine-containing polymers with extreme-temperature utility and oil- or chemical-resistance we have continued to explore combinations of polymerization catalysts and fluorine-containing monomers. During the period covered by this report the following types of polymerization systems have been studied:

| <u>Monomer</u> | <u>Catalyst</u> | <u>Reaction Medium</u> |
|-------------------------------------------|------------------------------------------------------------------------------|------------------------|
| Fluorinated olefin, acetylene or diene | Rhodium salts | Emulsion |
| Fluorinated olefin, acetylene or diene | Iridium salt or complex | Emulsion |
| Fluorinated diene and/or olefin | Ziegler catalyst, e.g. $\text{TiI}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$ | Hydrocarbon |

The principal studies have been made with diene monomers because of their greater reactivity relative to nonconjugated dienes or monomers containing only one double bond. The use of the noble metal catalysts, e.g. rhodium chloride, has led to the preparation of high molecular weight diene copolymers in good yield. Monomer syntheses were required and results of polymerization experiments are discussed below for each of the polymerization systems.

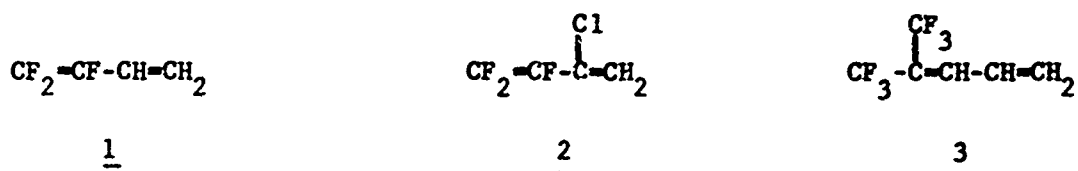
In addition, some further results are reported for the chemical modification of the readily available polymer cis-polybutadiene to provide elastomers having improved chemical and physical properties.

2. Rhodium Salt-initiated Emulsion Polymerization of Fluorine-containing Dienes

a. Polymerization

The UNIROYAL Corporate Research Center discovered the unique ability of rhodium salts to cause the stereospecific trans polymerization of butadiene^{1,2}. We have now used rhodium chloride as catalyst to survey the reactivity of a range of fluorinated monomers in this type of controlled structure polymerization. Table I shows that the conjugated dienes 1,1,2-tri-

fluorobutadiene (1), 1,1,2-trifluoro-3-chlorobutadiene (2) and 5,5,5-trifluoro-4-trifluoromethylpentadiene-1,3 (3) are readily polymerized by rhodium chloride

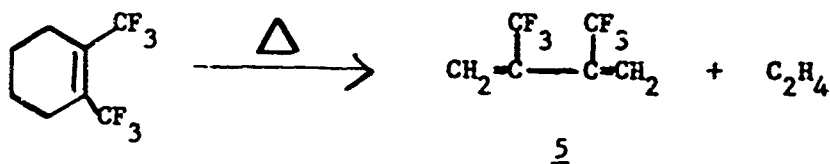


in aqueous emulsion. The polymers obtained had the following properties: poly-1, resin, Tg -35°C.; poly-2, rubber, Tg -17°; and poly-3, resin, m. p. 112°.

Exploratory polymerizations of unsaturated fluorine compounds other than conjugated dienes showed them to be much less reactive with the rhodium initiator. The results of these latter experiments, which are presented in detail in Table I, are briefly summarized as follows:

| <u>Monomer</u> | <u>% Conversion to Polymer</u> |
|------------------------------------------------------|--------------------------------|
| 3-Chloro-3,4,4-trifluoro-2-isopropenyl-cyclobutene-1 | 18 |
| α,β -Trifluorostyrene | 3 |
| 2,2,2-Trifluoroethyl vinyl ether | 0 |
| 2-Chloro-2,3,3-trifluorovinylcyclobutane | 0 |
| 1,2-Bis(trifluoromethyl)-4-methylcyclohexadiene-1,4 | 0 |
| 1,1,2-Trifluoromethyl-1,4-pentadiene | 0 |
| 1,1,2-Trifluoro-2-chloro-3-methyl-3-ethylcyclobutane | 0 |

Monomer 5 is of interest because its free radical-initiated homopolymer has been reported to have good high-temperature stability³. It was prepared by pyrolysis of the precursor obtained as described in our last report⁴.



Copolymerizations of butadiene (4) or monomer 5 with monomers 1, 2 and 3 initiated by rhodium trichloride in aqueous emulsion were studied as possible means of obtaining rubbers with lowered Tg values. These polymerizations are described in detail in Table II. The most successful ones are summarized below.

| <u>Monomer Pair</u> | <u>Mole-% of First Monomer in Polymer</u> | <u>Tg, °C.</u> |
|---------------------|-------------------------------------------|----------------|
| <u>1-4</u> | 51.4 | -48 |
| <u>2-4</u> | 55.1 | -35 |
| <u>3-4</u> | 9.8 | -20 |
| <u>5-4</u> | 31.9 | -27 |
| <u>2-1</u> | 51.4 | -2 |

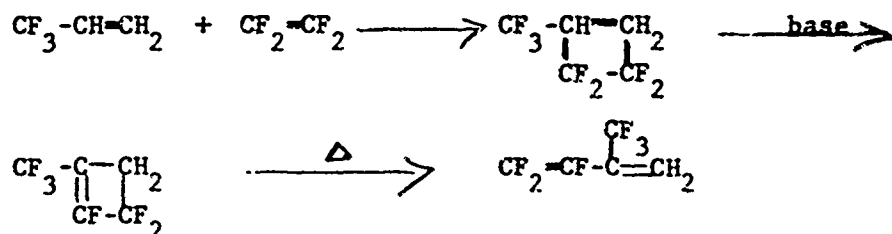
Since rhodium-initiated polybutadiene has the trans configuration, it might be expected that the butadiene units of the fluorodiene copolymers and the fluorodienes themselves also have the trans configuration. Preliminary studies of the microstructure of the copolymers have been made using infrared spectroscopy to determine cis, trans and vinyl contents of the butadiene portion¹⁴ and n. m. r. to establish the presence or absence of unsaturation on certain carbon atoms of the fluorinated monomers. The results are suggestive of trans-1,4 polymerization but further study on polymers and model compounds needs to be done before unequivocal structure assignments can be made. For instance, it is puzzling that the 3-4 copolymer has a Tg as high as -20° when it is known that trans-polybutadiene has Tg = -80°. It is possible that a significant amount of vinyl monomer unit is present, but again a further study of spectra-structure correlation must be made to establish the answer.

The monomer pair 5 and 4 was tested at a feed ratio of 1:2 and gave a polymer with nearly the same ratio of combined monomers. All the other monomer pairs were used at a 1:1 feed ratio and gave polymers of about a 1:1 monomer ratio except in the case of the monomer 3 and 4 combination. Monomer 3 appears much less reactive than the others, perhaps because it is highly unsymmetrical both from electronic and steric viewpoints.

It has been reported that formic acid promotes the rhodium-initiated polymerization of butadiene¹², but we have found it to be deleterious in the case of copolymerization of 1 and 4. Methylene chloride in the organic phase of the emulsion has a slightly favorable effect. Other organic solvents will be examined as well.

A small sample of the 1-4 copolymer was furnished to the U. S. Army Natick Laboratories for evaluation and larger quantities will be made for further testing.

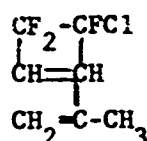
We are exploring the following cycloaddition route to the highly fluorinated monomer 1,1,2-trifluoro 3-(trifluoromethyl)butadiene which we consider to have potential in rhodium-initiated polymerization.



The initial attempts at the first step were unsuccessful. The cycloaddition reaction was carried out in solvent at pressures of 100 psig or less. This will be repeated without solvent at higher pressures since the literature reports this reaction to proceed under such conditions⁷.

3. Iridium-initiated Polymerizations of Fluorine-containing Dienes

Other work in this Laboratory has shown the effectiveness of iridium catalysts in polymerizing norbornenes¹¹. The close relationship of iridium to rhodium suggested that the iridium catalysts might also be active in polymerization of the fluorinated dienes. A representative group of fluorinated monomers was tested for polymerizability with iridium catalysts in aqueous emulsion. These experiments are summarized in Table III. As was the case with rhodium catalysts, significant conversions were obtained only with dienes. One comparison was made of the efficacies of ammonium iridium chloride and bis(1,4-cyclohexadienechloroiridium) as catalyst for the polymerization of monomer 6. The salt gave about four times as much polymer



6

as did the complex. The iridium salt is comparable in activity to rhodium chloride with monomer 6, but much slower than rhodium chloride with monomer 3.

4. Ziegler Catalyst-initiated Polymerizations of Fluorine-containing Dienes

As indicated in our previous report⁴ the monomers which appear most reactive with Ziegler-type catalysts (e.g. Ti- or V- based catalysts) are conjugated dienes. We have examined these monomers further in both homopolymerizations and copolymerizations using catalysts which are known to be effective in forming cis-polybutadiene.

a. 2-(Trifluoromethyl)butadiene

This monomer was prepared as described previously⁴ and used in a series of copolymerizations summarized below and described in detail in Table IV.

| <u>Comonomer</u> | <u>Catalyst Base</u> | <u>Conversion, %</u> | <u>Type of Polymer</u> |
|------------------|----------------------|----------------------|---------------------------------------------------------|
| <u>4</u> | Co octoate | 52 | High <u>cis</u> 1,4 content rubber, about 10% F monomer |
| <u>4</u> | Ti(OBu) ₄ | 4 | Fluid, viscous, mainly F monomer |
| <u>4</u> | TiI ₄ | <0.5 | High <u>trans</u> resin, about 15% F monomer |
| Ethylene | VOCl ₃ | 38 | resin |

The result with the cobalt-based catalyst is sufficiently interesting to warrant further study of this monomer when more is available.

In our version of the Et₃Al₂Cl₃-cobalt octoate system (115-1, Table VII) we have encountered crosslinking, as well as low cis content and high vinyl. Reduction of the cobalt concentration toward the Al/Co mole ratio of 500/1 used by Gippin at 5°⁶, speeded up the polymerization and gave immediate improvement in cis content. The reaction mixture attained incipient gelation in five minutes. This type of recipe is supposed to be operable with benzene containing 5 weight % butadiene. We are confident that a more suitable balance for screening purposes can be found by adjusting the ratio of catalyst components, their total amount and the amount of solvent.

b. 5,5,5-Trifluoro-4-trifluoromethyl-1,3-pentadiene (3)

This monomer, which was prepared as described previously⁴, was found to be unreactive toward the Ziegler-type catalysts as shown in Table V. It was shown in the same series of experiments that the cobalt-based catalyst was highly active in polymerizing butadiene. Thus there is a consistent picture of unreactivity of 3 with both the rhodium and Ziegler catalysts.

c. 2,3-Bis(trifluoromethyl)butadiene (5)

This diene appeared surprisingly unreactive in copolymerizations with ethylene or butadiene initiated by Ziegler catalysts (Table VI) in view of its ready copolymerization with butadiene initiated by rhodium (Table II). However, it is not uncommon that olefins with branching on the olefinic carbons are sluggish to polymerize with Ziegler catalysts.

d. 1,1,2-Trifluoro-3-chlorobutadiene (2)

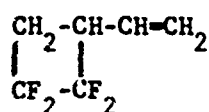
This compound was prepared by a method analogous to that used for 1,1,2-trifluorobutadiene^{4,5}. Its reactivity in attempted homopolymerizations with Ziegler catalysts (Table VII) was also much less than that which might have been expected from its ready copolymerizations with either butadiene or 1,1,2-trifluorobutadiene by rhodium catalysis.

e. 1,1,2-Trifluorobutadiene (1)

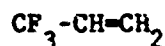
This diene was examined in a series of copolymerizations with butadiene listed in Tables VIII and IX. Use of the sesquiethyl aluminum sesquichloride and cobalt octoate catalyst gave copolymers of promising Tg (-82 to -84°) but with halogen content that is lower than what is believed necessary for good oil resistance. The cis-polybutadiene catalysts (TiI₂ or cobalt octoate) performed well in control experiments with butadiene but were much less active with the mixtures of 1 and butadiene. This result suggested the presence of an impurity in the sample of 1. Although previously prepared samples of 1 were pure by v. p. c. criteria, examination of the present batch showed a trace of butanol. This contamination was apparently sufficient to prevent polymerization by all but the cobalt catalyst and further illustrates the advantage of the rhodium-based catalyst in being insensitive to most polar impurities in the monomers.

5. Ziegler Catalyst-initiated Polymerizations of Fluorine-containing Olefins

A small number of experiments of this type was carried out. They are described in Table X and include copolymerizations of monomer 7 with butadiene and of monomer 8 with ethylene.



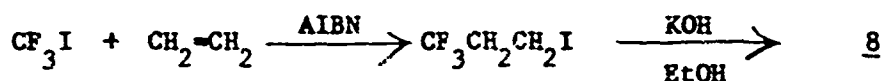
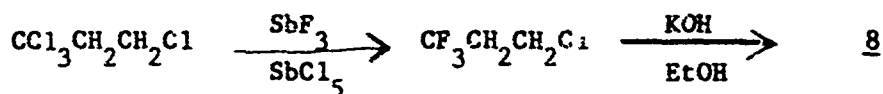
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8

Monomer 7 did not homopolymerize with either the $\text{Ti}(\text{OBU})_4$ or TiCl_4 -based catalysts. In a TiI_4 - or cobalt octoate-initiated copolymerizations with butadiene, high cis polymers containing only a little fluorine were obtained.

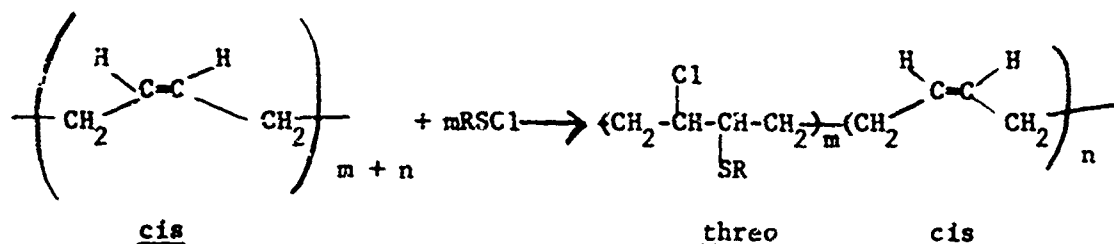
Monomer 8 was not commercially available at the time these polymerizations were carried out, therefore it was made by the following routes:



Monomer 8 was only slightly reactive in a $\text{VOCl}_3 + \text{Et}_3\text{Al}_2\text{Cl}_3$ -initiated copolymerization with ethylene. Analytical results for this copolymer are contradictory; microanalysis indicates 17% fluorine, whereas infrared spectroscopy suggests 1% or less. It is possible that the product is inhomogeneous and the polymerization will be rerun when more of monomer 8 is available.

6 Chemical Modification of cis-Polybutadiene

The very low glass transition temperature of cis-polybutadiene ($T_g = -108^\circ\text{C}.$) suggested that a rubber meeting the goals of this contract might be prepared from it by adding to the carbon-carbon double bonds one or more reagents which would improve the oil resistance. Our previous reports^{4,9} have described the facile addition of several sulfonyl chlorides to cis-polybutadiene to form adducts according to the following equation:



$$\% \text{ Saturation} = \frac{m}{m+n} \times 100$$

The threo configuration of the adduct sites is assigned on the basis of the trans orientation of addition observed in sulfenyl chloride reactions with cyclic olefins¹³ and the cis configuration of the unreacted sites is based on the infrared spectrum of the adduct. Thus the adduct has stereospecificity in its microstructure but a random macrostructure derived from the random location of the sites of addition along the chain. The result is a disappearance in the adduct of the crystallization (-64°C.) and melting (-21°C.) phenomena characteristic of cis-polybutadiene. During the period covered by this report a new adduct containing 30% of the theoretical amount of trifluoromethanesulfenyl chloride and additional quantities of other less-saturated adducts have been prepared for evaluation at the U. S. Army Natick Laboratories. The T_g values for these adducts are summarized below:

Glass Transition Temperatures (°C.) for Adducts
of cis-Polybutadiene and Sulfenyl Chlorides

| Addend | % Saturation | | | | |
|------------------------------------|--------------|-------|------|------|------|
| | 10 | 15 | 20 | 25 | 30 |
| CF ₃ SCl | -92 | -84* | -75 | -68 | -44* |
| C ₆ F ₅ SCl | -90 | -80** | -66* | -52* | - |
| CCl ₃ SCl | -85 | -50 | +28 | - | - |
| C ₆ Cl ₅ SCl | -99 | -50* | +18 | - | - |

* Submitted to Natick Laboratories for evaluation May 19, 1967.

** Previously evaluated at Natick Laboratories, see our previous report⁴.

Inspection of the data above shows that the fluorinated sulfenyl chlorides have a less deleterious effect on Tg than do the chlorinated sulfenyl chlorides. For the same reason the aliphatic sulfenyl chlorides are preferable to the aromatic analogs. Work in our laboratory and at Natick has shown these adduct rubbers can be successfully sulfur cured; their utility in meeting the goals of this contract would appear to depend on having adequate oil resistance.

EXPERIMENTAL

1. Monomer Synthesis

a. Pyrolysis of 1,2-bis(Trifluoromethyl)cyclohexene to 2,3-bis(Trifluoromethyl)-1,3-butadiene

A Vycor reaction tube of 22 mm. I. D. was packed with quartz rods and heated to 815-830°C. over a 12-in. length. A vacuum of 3 to 6 mm. was maintained during addition of 57.6 g. (.246 m.) 1,2-bis(trifluoromethyl)cyclohexene (93.2% purity by VPC) over a period of five hours. A condensate of 3.5 g. was obtained in the collection flask at room temperature, while the two dry-ice traps contained 12.7 g. and 1.6 g. for a total of 17.8 g. The traps were rinsed with cold trichlorobenzene to give 91.9 g. solution to which was added 0.2 g. *t*-butyl catechol. The mixture was stored in dry-ice and distilled three days later in a 12-inch packed column.

| <u>Fraction No.</u> | <u>Weight, grams</u> | <u>B. P., °C.</u> | <u>n²¹_D</u> | <u>% Diene (by VPC)</u> | <u>Yield, %</u> |
|---------------------|----------------------|-------------------|-----------------------------------|-------------------------|-----------------|
| 1 | 0.1 | | - | - | |
| 2 | 2.4 | 52-58 | 1.3388 | 83.7 | 5.2 |
| 3 | 0.6 | 70-74 | 1.4040 | 31.7 | |
| 4 | 1.3 | 83-86 | 1.4058 | - | |
| 5 | 2.0 | 112-135 | 1.4010 | | |
| 6 | 3.0 | 178-198 | 1.4972 | | |
| 7 | 4.0 | 198-200 | 1.5557 | | |
| 8 | 9.5 | 213 | 1.5680 | | |
| | | Residue | 1.5692 | | |

A second reaction run at 725°C. under 3-5 mm. gave 15.4 g. (54%) of product which was 96% pure.

b. 1,1,2-Trifluoro-3-chloro-1,3-butadiene

In a one-liter 3-neck flask were placed 62.3 g. (0.865 m.) 90% zinc dust, 1.4 g. zinc chloride, and 118.7 g. *n*-butanol. The mixture was heated to 84°C. with agitation under 250-300 mm. vacuum. Addition of 48.3 g. (0.188 m.) 3,4,4-trifluoro-4-bromo-2,3-dichlorobutene-1 (Pierce Chemical, 96.7% purity) was carried out over 20 minutes and 63.6 g. of condensate was trapped with a dry-ice condenser (59A). Another 47.8 g. (0.185 m.) of the dichloro compound was added over 43 minutes to give 48.0 crude product. A second dry-ice trap used in both runs contained 11.4 g. (21.5%) of crude diene.

The three main fractions were combined and distilled at 40-60°C. pot temperature and 75-150 mm. There was obtained 34.3 g. (64%) of diene which was redistilled through a 12-inch long packed column at 184-188 mm. to give 17.2 g. (30%) of the diene of 92.8% purity. The major impurities were 4.8% of a low boiler and 0.5% of a high boiler believed to be n-butanol.

c. 3,3,3-Trifluoropropyl Chloride

In a 5-l 3-necked stainless steel flask were placed 500 g. (2.80 moles) of Peninsular ChemResearch antimony trifluoride and 112 g. of antimony pentachloride. There was an exotherm from 16° to 38°. The mixture was warmed to 49° and 252.3 g. (1.39 moles) of 1,1,1,3-tetrachloropropane was added over a period of three and one-third hours. During this time the flask temperature was 65-88° and gentle reflux occurred. Volatile products formed during the reaction were collected in a Dry-Ice condenser and were combined with the material distilled off when the flask temperature was raised to 110°. The crude product was washed with 7.5 N hydrochloric acid and redistilled to give 43.6 g. (27%) of 3,3,3-trifluoropropyl chloride, b. p. 44-47°, n_D^{20} 1.3280-1.3282.

V. p. c. analysis of the product showed it to be 98.2% pure with 1.4% of a more volatile component.

d. 3,3,3-Trifluoropropyl Iodide

In a 750-ml. stainless steel bomb were placed 1.2 g. azobisisobutyronitrile and 250 g. of methanol. The bomb atmosphere was replaced with nitrogen by five times evacuating to 0.2 mm. and refilling with nitrogen to 20 psig at Dry Ice temperature. The bomb was reevacuated and charged with 133 g. (0.682 mole) of Peninsular ChemResearch trifluoromethyl iodide.

The bomb was stirred and heated at 66-67° with incremental addition of ethylene whenever the pressure dropped to 80 psig. The total ethylene uptake was 29 g. (152% of theory for a 1:1 adduct). The bomb was cooled and the methanol solution diluted with 1000 ml. of water to give 114.6 g. of heavy oil which was 86% 3,3,3-trifluoropropyl iodide by v. p. c. Distillation through a 12-in. packed column gave product, b. p. 88-89°, n_D^{25} 1.4170, 99.5% pure by v. p. c.

e. 3,3,3-Trifluoropropene

(1) By dehydrochlorination of 3,3,3-trifluoropropyl chloride

A solution of 17.8 g. (0.134 mole) of 3,3,3-trifluoropropyl chloride in 69.2 g. of 95% ethanol was treated with 30 ml. of 1.7 N ethanolic potassium hydroxide followed by another 90 ml. after twenty minutes. The solution was heated to 67° during ninety minutes to give 11.5 g. of volatile product collected in a Dry Ice condenser. Distillation of the crude product gave 10.9 g. (85%) of 3,3,3-trifluoropropene, b. p. -22°.

A second reaction gave 11.4 g. (89%) of product, b. p. -22°.

(2) By dehydroiodination of 3,3,3-trifluoropropyl iodide

The method described above gave 78% yield of the olefin, b. p. -22°, when applied to the corresponding iodo compound.

f. 1,1,2,2-Tetrafluoro-3-vinylcyclobutane

The cycloaddition of butadiene and tetrafluoroethylene was carried out under conditions similar to those reported⁸ except a solvent (240 g. o-dichlorobenzene) was used, reducing the pressure of 85 g. (1.57 moles) of butadiene and 38 g. (0.38 mole) of tetrafluoroethylene in a 750-ml. stainless steel bomb to less than 200 psig. The solution was heated eight hours at 130°, cooled and distilled to give 40 g. (68%) of adduct containing 3% of butadiene as determined by v. p. c.

2. Polymerizations

The rhodium- and iridium-initiated polymerizations were carried out by the aqueous emulsion technique described by Rinehart, Smith, Witt and Romeyn^{1,2}.

Polymerizations initiated by Ziegler-type catalysts were run by the vacuum line technique described in our earlier reports^{4,9}.

3. Chemical Modification of *cis*-Polybutadiene

a. Materials

Trifluoromethanesulfonyl chloride was obtained from Peninsular ChemResearch. Pentafluoro- and pentachloro-benzenesulfonyl chlorides were prepared by the method of Almasi and Gants¹⁰.

b. Addition Reactions

These were carried out as described in an earlier report⁹.

PROPOSED WORK

1. In the rhodium- and iridium-catalyzed emulsion polymerizations of fluorinated dienes, study the effect of feed ratio, temperature, solvent, etc. on microstructure and monomer combining ratio. Control of these two dependent variables will permit us to design polymers meeting the Contract objectives.
2. Follow up the lead on cobalt-catalyzed copolymerizations by screening other monomer pairs and studying effect of feed ratio, solvent, temperature, etc.
3. Prepare additional fluorinated diene copolymers for further evaluation.
4. Continue synthetic work to prepare 1,1,2-trifluoro-3-(trifluoromethyl)butadiene and other monomers as needed.
5. Prepare low-temperature rubbers by other chemical modifications of cis-polybutadiene. Prepare additional amounts of adducts as may be required for evaluation.

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TABLE I

SURVEY OF HOMOPOLYMERIZABILITY OF VARIOUS FLUORINATED MONOMERS IN EMULSION BY RHODIUM CHLORIDE

| Experiment No. | 96-1 | 97-1 | 97-2 | 97-3 | 97-4 | 103-1 | 103-2 | 103-3 | 103-6 | 119-1 |
|----------------------------------------------------------------|--------|------|-------|-------|------|---------------|-------|--------------|----------------|-------|
| Rhodium Chloride trihydrate, g. | .020 | .020 | .020 | .020 | .020 | .020 | .020 | .020 | .020 | .020 |
| Distilled Water, ml. | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
| 20% Naacconol NRSF, ml. | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 1,1,2-Trifluorobutadiene, mmoies | 64.5 | - | - | - | - | - | - | - | - | - |
| B,B,β-Trifluoroethyl vinyl ether, mmoles | - | 25 | - | - | - | - | - | - | - | - |
| α,A,β-Trifluorostyrene, mmoles | - | - | 25 | - | - | - | - | - | - | - |
| 1,1,2-Trifluoro-2-chloro-3-vinyl cyclobutane, mmoles | - | - | - | 25 | - | - | - | - | - | - |
| 4,5,5-Trifluoro-1,4-pentadiene, mmoles | - | - | - | - | 25 | - | - | - | - | - |
| 1,1,2-Trifluoro-2-chloro-3-isopropenylcyclobut-3-ene, mmoles | - | - | - | - | - | 21.4 | - | - | - | - |
| 1,1,2-Trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane, mmoles | - | - | - | - | - | - | 20 | - | - | - |
| 1,2-Bis(trifluoromethyl)-4-methyl-1,4-cyclohexadiene, mmoles | - | - | - | - | - | - | - | 25 | - | - |
| 5,5,5-Trifluoro-4-trifluoromethyl-1,3-pentadiene, mmoles | - | - | - | - | - | - | - | - | 25 | - |
| 1,1,2-Trifluoro-3-chlorobutadiene, mmoles | - | - | - | - | - | - | - | - | - | 20.8 |
| (added as a solution 31% by weight in benzene) | | | | | | | | | | |
| Polymerization time at 50°C., hrs. | 67 | 162 | 42 | 42 | 162 | 65 | 65 | 65 | 65 | 65 |
| Yield, g. | 6.915 | 0 | .134 | trace | 0 | .817 | .051 | 0 | 4.00 | 3.059 |
| Conversion, % | 100 | 0 | 3 | 0 | 0 | 18 | 1+ | 0 | 84 | 100 |
| X-ray crystallinity | slight | - | - | - | - | amorph.slight | - | amorph. | - | - |
| Product Appearance | resin | - | resin | - | - | resin resin | - | resin rubber | - | - |
| C/C ₃ Solubility | partly | - | - | - | - | - | - | - | swells soluble | - |
| Tg, °C. | -35 | - | - | - | - | - | - | - | - | -17 |
| Tm, °C. | 56.79 | - | . | - | - | - | - | - | 112 | - |

Table II

Copolymerization of Fluorinated Dienes with Butadiene or Fluorinated Dienes in Emulsion with Rhodium Catalysts

| Experiment No. | 99-1 | 99-2 | 99-3 | 99-4 | 104-3 | 103-4 | 108-2 | 104-1 | 108-1 | 114-1 | 119-2 | 103-5 | 104-2 | 119-3 |
|----------------------------------------------------------|-----------------|--------|--------|--------|--------|---------|----------|------------|----------|--------|-------------------|--------|--------|-------------------|
| Rhodium chloride trihydrate, g. | .020 | .020 | .020 | .020 | - | .020 | .020 | - | - | .020 | .020 | .020 | - | .020 |
| Bis(1,4-cyclohexadiene chlororhodium), g. | - | - | - | - | .05 | - | - | .05 | .05 | - | - | - | .05 | - |
| Distilled water, ml | 7 | 7 | 7 | - | 13 | 7 | 7 | 13 | 13 | 7 | 7 | 7 | 13 | 7 |
| 20% Nacconol NRSF, ml. | 1 | 1 | 1 | - | 2.5 | 1 | 1 | 2.5 | 2.5 | 1 | 1 | 1 | 2.5 | 1 |
| Formic acid, ml. | - | .25 | - | - | 5 | - | - | 5 | 5 | - | - | - | 5 | - |
| Methylene chloride, ml. | - | - | 5 | 15 | 5 | - | - | 5 | - | 5 | - | - | 5 | - |
| 5,5,5-Trifluoro-4-trifluoro-methyl-1,3-pentadiene, mmols | - | - | - | - | - | 25 | 18 | 25 | 18 | - | - | 25 | 25 | - |
| 2,3-Bis(trifluoromethyl)butadiene, mmols | - | - | - | - | - | - | - | - | - | 11.7 | - | - | - | - |
| 1,1,2-Trifluoro-3-chloro-butadiene, mmols | - | - | - | - | - | - | - | - | - | - | 20.8 | - | - | 20.8 |
| 1,1,2-Trifluorobutadiene, mmols | 21.5 | 21.5 | 21.5 | 21.5 | 21.5 | - | - | - | - | - | - | 21.5 | 21.5 | 21.5 |
| Butadiene, mmols | 21.5 | 21.5 | 21.5 | 21.5 | 21.5 | 21.5 | 21.5 | 21.5 | 21.5 | 21.5 | 21.5 | - | - | - |
| Polymerization time at 50°C., hrs. | 17 | 17 | 17 | 143 | 65 | 65 | 115 | 64 | 283 | 18 | 65 | 65 | 65 | 65 |
| Yield, g. | 1.498 | .455 | 2.068 | 0 | .628 | .70+ | 1.695 | 1.343 | 1.5+ | .490 | 2.548 | 6.44 | 2.508 | 5.126 |
| Conversion, % | 43 | 13 | 59 | 0 | 18 | ? | 37 | 28 | 32+ | 14.5 | 60 | 91 | 42 | 97 |
| Product | (brown rubbers) | - | - | - | rubber | rubber | rubber | dark resin | resin | nervy | nervy | rubber | tough | tough |
| | tough | soft | tough | - | logey | 2 kinds | leathery | resin + | leathery | rubber | rubber | white | rubber | rubber |
| | nervy | - | nervy | - | - | I.R.'s | - | syrup | - | - | - | tough | sl. | sl. |
| | | | | | | alike | | | | | | | | sticky |
| Solubility in CHCl_3 | swells | swells | swells | swells | swells | swells | swells | swells | swells | swells | swells | swells | swells | swells |
| % Fluorine | 32.9 | 32.3 | 35.8 | 35.03 | 35.03 | 35.03 | 16.63 | - | - | 37.3 | 19.0 ^a | 56.5 | 55.3 | 14.5 ^a |
| Mole % F monomer | 45.4 | 44.1 | 51.4 | 45.7 | 45.7 | 45.7 | 9.8 | - | - | 31.9 | 55.1 | 90.5 | 87.1 | 51.4 |
| Tg, °C. | -47 | - | -48 | -48 | -48 | -48 | -20 | - | - | -27 | -35 | -17 | +2 | -25 |
| Tg, °C. | +58 | - | +58 | +55 | +55 | +55 | +55 | +69 | +69 | - | - | +103 | 108 | - |

^a. % Chlorine

Table III

| Homopolymerization of Various Types of Fluorinated Monomers in Emulsion with Iridium Catalysts - 240 hrs. at 50°C. | | | | | | | | | | All polymerizations run | |
|--------------------------------------------------------------------------------------------------------------------|-------------|-------------|------------|-------|-------|-------|-------|-------|-------------|-------------------------|--|
| Experiment No. | 106-1 | 106-2 | 106-3 | 106-4 | 106-5 | 106-6 | 106-7 | 106-8 | 106-9 | 106-10 | |
| Ammonium iridium chloride, g. | .075 | .075 | .075 | .075 | .075 | .075 | .075 | .075 | .075 | | |
| Bis(1,4-cyclohexadiene chloroiridium), g. | - | - | - | - | - | - | - | - | - | | |
| Distilled water, ml. | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | |
| 20% Novulphor C, ml. | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | |
| 20% Aquarex ME, ml. | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | |
| 40% Formaldehyde, ml. | .5 | .5 | .5 | .5 | .5 | .5 | .5 | .5 | .5 | .5 | |
| 3-Chloro-3,3,4-trifluoro-2-isopropenyl cyclobutene-1, mmoles | 25 | - | - | - | - | - | - | - | - | 25 | |
| 1,1,2-Trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane, mmoles | - | 25 | - | - | - | - | - | - | - | - | |
| 1,2-Bis(trifluoromethyl)-4-methyl-1,4-cyclohexadiene, mmoles | - | - | 25 | - | - | - | - | - | - | - | |
| 1,1,2-Trifluoro-2-chloro-3-methyl-3-(3,3,4-trifluoro-4-chlorocyclobutenyl)cyclobutene, mmoles | - | - | - | 25 | - | - | - | - | - | - | |
| α,β -Trifluorostyrene, mmoles | - | - | - | - | 25 | - | - | - | - | - | |
| 1,1,2-Trifluoro-2-chloro-3-vinyl cyclobutane, mmoles | - | - | - | - | - | 25 | - | - | - | - | |
| 1,1,2-Trifluoro-2-chloro-3-methyl-3-vinylcyclobutane, mmoles | - | - | - | - | - | - | 25 | - | - | - | |
| 2,2,2-Trifluoroethyl vinyl ether, mmoles | - | - | - | - | - | - | - | 25 | - | - | |
| 5,5,5-Trifluoro-4-trifluoromethyl-1,3-pentadiene, mmoles | - | - | - | - | - | - | - | - | 25 | - | |
| Yield, g. | 2.83 | .008 | .007 | - | - | - | - | - | .560 | .727 | |
| Conversion, % | 77 | <1 | <1 | - | - | - | - | - | 12 | 20 | |
| Product appearance | white resin | white resin | gray resin | - | - | - | - | - | white resin | white resin | |

Table IV

Polymerizations of 2-(Trifluoromethyl)butadiene with Ziegler Catalysts

| Experiment No. | 91-3 | 91-4 | 91-5 | 91-6 | 91-7 | 91-9 |
|------------------------------------------------------------------------|-----------------|------------------|-------------------------|---------------|---------------------------|--------|
| Dry benzene, ml. | 12.2 | 12.2 | 16 | 10 | - | - |
| Dry heptane, ml. | - | - | - | - | 15 | 15 |
| 1.25 M Al(i-bu) ₃ in benzene, ml. | .4 | .4 | - | - | - | - |
| 0.06 M Cobalt Octoate in benzene, ml. | - | - | 1 | - | - | - |
| 0.55 M Al(i-bu) ₃ in benzene, ml. | - | - | - | .55 | - | - |
| 0.05 M VOCl ₃ in heptane, ml. | - | - | - | - | 10 | 10 |
| Freeze in | < | dry ice | | > | < liquid N ₂ > | |
| Butadiene from vac. line, mmoles | 43 | 43 | 21.5 | - | - | - |
| 2-Trifluoromethyl butadiene, mmoles | - | 9.7 | 9.7 | 7.3 | 9.7 | - |
| Ethylene from vac. line, mmoles | - | - | - | - | 10.8 | 21.8 |
| Made homogeneous at °C. | 25 | 25 | 25 | 25 | 78 | no |
| 0.017 M Dow TiI ₄ in C ₆ H ₆ , ml. | 5.6 | 5.6 | - | - | - | - |
| 0.30 M Et ₃ Al ₂ Cl ₃ in heptane, ml. | - | - | 1 | - | 4.2 | 4.2 |
| 0.25 M Ti(OBu) ₄ in benzene, ml. | - | - | - | .4 | - | - |
| Shake & stir in air bath, min. | 15 | 15 | 15 | 15 | instant | |
| Exotherm | + | - | - | - | polymer | |
| Color after assembly | dark brown | cherry red | blue green | clear yellow | purple | purple |
| Polymerization time at 25°, hrs. | 68 | 68 | 67 | 67 | 17 | 17 |
| Yield, g. | 2.27 | .018 | 1.21 | .04 | .56 | .66 |
| Conversion, % | 98 | <.5 | 52 | 4 | 38 | 100 |
| Product | solid rubber | flaky soft resin | solid rubber (some gel) | viscous fluid | resin | resin |
| Composition | | | | | | |
| % cis by infrared | 73 ^a | - | 70 ^a | - | - | - |
| % trans by infrared | 23 ^a | 84 | 29 ^a | - | - | - |
| % vinyl by infrared | 4 ^a | - | 10 ^a | - | - | - |
| % C ₅ F ₃ H ₅ by infrared | - | 16 | 13 | (100) | 34 | - |
| 888 cm ⁻¹ possible -C(CF ₃)=CH ₂ | - | - | - | yes | - | - |
| 840 cm ⁻¹ possible -C=C(CF ₃)- ² | - | - | - | - | yes | - |
| % C ₅ F ₃ H ₅ baxed on F | - | - | 4.8 | - | 6.4 | - |
| X-ray crystallinity % | - | - | - | - | 37 | - |

a. Normalized to 100%.

Table V

Polymerizations of 5,5,5-Trifluoro-4-trifluoromethyl-1,3-pentadiene
with Ziegler Catalysts

| Experiment No. | 92-2 | 92-3 | 92-6 | 92-7 | 92-8 | 94-5 | 94-6 |
|------------------------------------------------------------------|---------------------|------|-------|--------|-----------------|---------------------|----------------|
| Dry benzene, ml. | 5 | 5 | 4 | 4 | 10 | - | - |
| Dry heptane, ml. | - | - | - | - | - | 15 | 23 |
| 1.25 M Al(i-Bu) ₃ , ml. | .4 | .4 | - | - | - | - | 2 |
| 0.06 M CoOctoate, ml. | - | - | 1 | 1 | 1 | - | - |
| 0.05 M VOCl ₃ , ml. | - | - | - | - | - | 10 | - |
| CH ₂ =CH-CH-C(CF ₃) ₂ , mmoles | 11.6 | 11.6 | 11.6 | 11.6 | - | 25 | 25 |
| Seal | | | | | | | |
| Freeze in | - | - | - | - | CO ₂ | N ₂ | N ₂ |
| Butadiene, mmoles | - | - | - | - | 21.5 | - | - |
| Ethylene, mmoles | - | - | - | - | - | 11.2 | 11.2 |
| Condition to 25°C. | yes | yes | yes | yes | yes | - | - |
| Condition to 5°C. | - | - | - | - | - | yes | yes |
| 0.25 M Ti(OBu) ₄ , ml. | .4 | .4 | - | - | - | - | - |
| 0.30 M Et ₃ Al ₂ Cl ₂ , ml. | - | - | 1 | 1 | 1 | 4.2 | - |
| 0.25 M VO(OBu) ₃ , ml. | - | - | - | - | - | - | 2 |
| Stir 15' at 25°, run at 25° | - | yes | - | yes | yes | yes | yes |
| Shake & run at 60° | yes | - | yes | - | - | - | - |
| Exotherm | - | - | - | - | + | - | - |
| Catalyst color | < yellow brown > | | gray | bluish | greenish | purple | yellow |
| | | | green | green | | | |
| Time, hrs. | 19 | 19 | 19 | 19 | 19 | 16 | 16 |
| Yield, g. | (.016 gm. combined) | | .010 | 0 | 1.10 | .25 | .26 |
| Conversion, % | <1 | <1 | <1 | 0 | 95 | 5 | 5 |
| X-ray crystallinity | - | - | - | - | - | (like polyethylene) | |
| % F | - | - | - | - | - | 3.61 | 1.36 |
| Mole-% C ₆ H ₄ F ₆ in polymer | - | - | - | - | - | 6.02 | 2.27 |

Table VI

Copolymerizations of 2,3-Bis(trifluoromethyl)butadiene
with Ziegler Catalysts

| Expt. No. | 94-1 | 94-2 | 94-3 | 94-4 |
|-----------------------------------------------------------------------------------|-----------------------|------------------|--------------------------------------------------------|----------------------|
| Dry benzene, ml. | 12.2 | 16 | - | - |
| Dry heptane, ml. | - | - | 15 | 23 |
| 1.25 M Al(<u>i</u> -bu) ₃ , ml. | .4 | - | - | - |
| .06 M Co octoate, ml. | - | 1 | - | - |
| .05 M VOCl ₃ in heptane, ml. | - | - | 10 | - |
| CH ₂ =C(CF ₃)-C(CF ₃)=CH ₂ , mmoles | 20 | 20 | 20 | 20 |
| Seal & freeze | | | | |
| Butadiene, mmoles | 21.8 | 21.8 | - | - |
| Ethylene, mmoles | - | - | 11.5 | 11.5 |
| Condition to | 25° | 25° | 5° | 5° |
| .018 M TiI ₄ , ml. | 5.6 | - | - | - |
| .30 M Et ₃ Al ₂ Cl ₃ , ml. | - | 1 | 4.2 | - |
| .25 M VO(OEt) ₃ , ml. | - | - | - | 2 |
| Polymerize at 25°, hrs. | 46 | 46 | 16 | 16 |
| Yield, gms. | .004 | .63 | .293 | .281 |
| Conversion, % | <1 | 13 | 7 | 7 |
| | brown oily scum | sticky rubber | brown-white resin | brown-white resin |
| X-ray crystallinity | - | - | (resemble polyethylene except 4.50A line is weaker) | |
| Infrared | | | (polyethylene & faint F at 1130 cm ⁻¹) | |
| % F Schwarzkopf | - | 5.72 | 1.91 | 1.71 |
| % CH ₂ =C(CF ₃)-C(CF ₃)=CH ₂ | - | 9.54 | 3.18 | 2.85 |
| Butadiene portion | | | | |
| % cis | - | 79 | - | - |
| % vinyl | - | 13 | - | - |
| % trans | - | 8 | - | - |

Table VII
Polymerizations of 1,1,2-Trifluoro-3-chlorobutadiene with Ziegler Catalysts

| Expt. No. | <u>119-4</u> | <u>119-5</u> |
|-----------------------------------------------------------|-----------------|----------------|
| <u>Apparatus</u> | | |
| 250 ml. stainless steel bomb | + | |
| 100 ml. pyrex reaction tube | | + |
| <u>Reagents</u> | | |
| Dry heptane, ml. | 13.3 | 8.3 |
| Dry benzene, ml. | - | - |
| 0.05 M VOCl_3 , ml. | 10 | 10 |
| 1,1,2-Trifluoro-3-chlorobutadiene, mmoles ^a | 4.1 | 10.5 |
| 0.30 M $\text{Et}_3\text{Al}_2\text{Cl}_3$, ml. | 4.2 | 4.2 |
| Shake behind safety screen | yes | yes |
| Polymerization time at 25°C., hrs. | 66 | 66 |
| Yield, g. | .069 | .355 |
| Conversion, % | 12 | 24 |
| Product | lt. brown resin | lt brown resin |
| X-ray crystallinity | - | amorphous |

a. Added as a solution 31% by weight in benzene

Table VIII

Attempted Copolymerization of Butadiene and 1,1,2-Trifluorobutadiene
Comparison of Benzene and Methylene Chloride Using a Cobalt Catalyst

| Experiment No. | 102-1 | 102-2 | 102-3 | 102-4 | 102-6 | 102-5 |
|--------------------------------------------------------------|------------|-----------------------------|-------|----------|--------|-------|
| Dry benzene, ml. | 20 | 20 | 20 | - | - | - |
| Dry methylene chloride, ml. | - | - | - | 20 | 20 | 20 |
| 0.06 M CoOctoate, ml. | 2 | 2 | 2 | 2 | 2 | 2 |
| Seal, freeze in dry ice | | | | | | |
| Butadiene, mmoles | 22 | 33 | 11 | 22 | 33 | 11 |
| 1,1,2-Trifluorobutadiene, mmoles | 22 | 11 | 33 | 22 | 11 | 33 |
| Pressurize 4 psi N ₂ | | | | | | |
| Condition to 25°C. | | | | | | |
| 0.30 M Et ₃ Al ₂ Cl ₃ , ml. | 2 | → | | | | |
| Shake and stir at 25° | | | | | | |
| Polymerization time at 25°, hrs. | 16 | → | | | | |
| Exotherm | + | + | + | 0 | 0 | 0 |
| Viscosity of reaction mixture | medium | highest | low | low | lowest | low |
| | | some gel | | some gel | | |
| Yield, g. | 1.16 | 1.720 | .726 | 1.060 | 1.539 | .579 |
| Intrinsic viscosity in CHCl ₃ | .73 | - | - | .82 | - | - |
| Properties | < | all slightly sticky rubbers | | | | > |
| | | with poor cobalt cleanup | | | | |
| Conversion, % | 33 | 59 | 18 | 30 | 53 | 14 |
| Tg/Tm | -84 +57 | -82 +50 | | | | |
| Composition from Infrared ^a | | | | | | |
| % cis | 45 | 42 | 24 | 9 | 13 | 7 |
| % trans | 11 | 12 | 20 | 20 | 22 | 25 |
| % vinyl | 44 | 46 | 56 | 71 | 65 | 70 |
| % trifluorobutadiene | 31 | 22 | 44 | 34 | 34 | 60 |

a. Sum of % cis + % trans + % vinyl is normalized to 100%.

Table IX

Attempted Copolymerization of Butadiene and 1,1,2-Trifluorobutadiene
with Some Cis-Polybutadiene Catalysts

| Experiment No. | <u>116-3</u> | <u>116-4</u> | <u>116-7</u> | <u>116-8</u> |
|--------------------------------------------------------------|------------------------|---------------|--------------|--------------|
| Dry benzene, ml. | 16.2 | 8.3 | 16.2 | 8.3 |
| Dry heptane, ml. | - | 8.3 | - | 8.3 |
| 0.55 M Al(<u>i</u> -bu) ₃ , ml. | .37 | - | .37 | - |
| 0.06 M Cobalt octoate, ml. | - | .2 | - | .2 |
| Butadiene, mmoles | 32.25 | 32.25 | 32.25 | 32.25 |
| 1,1,2-Trifluorobutadiene, mmoles | - | - | 21.5 | 21.5 |
| 0.017 M TiI ₄ , ml. | 2.25 | - | 2.25 | - |
| 0.30 M Et ₃ Al ₂ Cl ₃ , ml. | - | 1 | - | 1 |
| Exotherm | + | + | - | + |
| Appearance | thick dark brown | light blue | red | yellow |
| Color | normal | normal | no | |
| Yield, g. | 1.554 | 1.833 | - | 1.723 |
| Infrared analysis ^a | | | | |
| % cis | 80.9 | 73.3 | - | 87.3 |
| % trans | 15.3 | 18.9 | - | 8.2 |
| % vinyl | 3.8 | 7.9 | - | 4.5 |
| F | - | - | - | 0 |

a. Sum of % cis + % trans + % vinyl is normalized to 100%.

Table X

Polymerization of Fluorinated Non-Dienes with Ziegler Catalysts

| Experiment No. | 112-5 | 112-6 | 112-7 | 112-4 | 112-9 | 111-1 | 105-1 |
|--------------------------------------------------------------------|-----------------|-------|-----------------|-----------------|-----------------|---------------------------------------|---------------------|
| Dry benzene, ml. | 10 | 10 | 12.2 | 10 | 16 | - | - |
| Dry heptane, ml. | - | - | - | - | - | 15 | 15 |
| 0.125 M Al(<i>i</i> -bu) ₃ , ml. | .4 | .4 | .4 | - | - | - | - |
| 0.06 M Cobalt octoate, ml. | - | - | - | 1 | 1 | - | - |
| 0.05 M VOCl ₃ in heptane, ml. | - | - | - | - | - | 10 | 10 |
| 1,1,2,2-Tetrafluoro-3-vinyl cyclobutane, mmoles | 25 | 25 | 25 | - | 25 | 50 | - |
| Seal, freeze in | - | - | CO ₂ | CO ₂ | CO ₂ | N ₂ | N ₂ |
| Butadiene, mmoles | - | - | 43 | 21.5 | 43 | - | - |
| 3,3,3-Trifluoropropene, mmoles | - | - | - | - | - | - | 5.38 |
| Ethylene, mmoles | - | - | - | - | - | 11.25 | 11.25 |
| Pressurize 4 psi dry N ₂ | | | | | | | |
| Condition to °C. | 25 | 25 | 25 | 25 | 25 | 5 | 5 |
| 0.25 M Ti(OBu) ₄ in C ₆ H ₆ , ml. | .4 | - | - | - | - | - | - |
| 0.5 M TiCl ₄ in C ₆ H ₆ , ml. | - | .2 | - | - | - | - | - |
| 0.017 M TiI ₄ , ml. | - | - | 5.6 | - | - | - | - |
| 0.30 M Et ₃ Al ₂ Cl ₃ , ml. | - | - | - | 1 | 1 | 4.2 | 4.2 |
| Catalyst color | yellow brown | black | dark brown | blue- green | blue- green | purple initially | purple initially |
| Exotherm | 0 | 0 | +++ | + | + | - | - |
| Polymerization time at 25°, hrs. | 64 | 64 | 43 | 65 | 43 | 18 | 64 |
| Yield, g. | 0 | 0 | 2.163 | 1.088 | 2.546 | .330 | .162 |
| Conversion, % | 0 | 0 | 32 | 94 | 37 | 4 | 20 |
| Product | - | - | soupy rubber | soft rubber | soft rubber | brown white resin | white resin |
| X-ray crystallinity | - | - | - | - | - | (resemble P.E.) | |
| % F | - | - | 0 | - | 0 | - | 16.92 ^a |
| % C ₃ H ₃ F ₃ | - | - | - | - | - | - | 10.5 |
| Infrared ^a | - | - | - | - | - | 88% P.E. + minor amt. F polymer | |
| cis | - | - | 75 | 67 | 60 | - | - |
| trans | - | - | 22 | 7 | 18 | - | - |
| vinyl | - | - | 4 | 26 | 22 | - | - |
| F | - | - | v.minor | - | minor | - | - |
| Solubility in CHCl ₃ | - | - | - | - | yes | - | - |
| Tg, °C. | - | - | -105 | - | -97 | - | - |

a. Sum of % cis + % trans + % vinyl is normalized to 100%.

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| 13 ABSTRACT Rhodium compounds were found to give good conversions of fluorinated dienes to polymers in aqueous emulsion systems. For example, a 51:49 copolymer (Tg -48°) of 1,1,2-trifluorobutadiene and butadiene was prepared in this way in 59% conversion in 17 hours at 50°C. Several of the copolymers are formed with monomer ratios approaching the feed ratios. Microstructure of these polymers has been examined in a preliminary way by means of infrared and n. m. r. measurements. Other catalyst and fluorinated-monomer combinations were screened for activity in homopolymerization and copolymerization. A number of fluorinated sulfonyl chloride-modified <u>cis</u> -polybutadienes and one rhodium initiated copolymer were prepared on a scale large enough for preliminary evaluation at the U. S. Army Natick Laboratories. | | |

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